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(21) International Application Number: PCT/EP99/08359 (22) International Filing Date: 2 November 1999 (02.11.99) (30) Priority Data: 2222/98 4 November 1998 (04.11.98) CH (71) Applicant (for all designated States except AT US): NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH). (71) Applicant (for AT only): NOVARTIS-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT M.B.H. [AT/AT]; Brunner Strasse 59, A-1230 Vienna (AT). (72) Inventors; and (75) Inventors/Applicants (for US only): KRÜGER, Christian [DE/DE]; Talstrasse 1, D-79639 Grenzach-Wyhlen (DE). ALLARD, Jean-Louis [FR/CH]; L'Orsastrasse 16, CH-4310 Rheinfelden (CH). LABHART, Christoph [CH/CH]; Muspenacker 305, CH-4204 Himmelried (CH). (74) Agent: BECKER, Konrad; Novartis AG, Corporate Intellectual Property, Patent & Trademark Department, CH-4002 Basel (CH).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HERBICIDAL COMPOSITION (57) Abstract Liquid herbicidal composition, containing a grass herbicide that is suspended or dissolved in a non-aqueous liquid phase, a herbicide of the sulfonylurea type that is suspended in a non-aqueous liquid phase, and at least one surface-active substance.		

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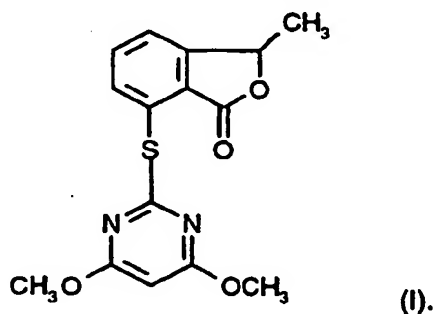
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Herbicidal composition

The present invention relates to a new liquid herbicidal composition, the preparation thereof, as well as the use of the composition in the control of undesired plant growth in crops of cultivated plants.

According to the present invention, a liquid herbicidal composition is proposed, which contains, in addition to customary formulation excipients, (a) at least one grass herbicide that is suspended or dissolved in a non-aqueous liquid phase, (b) at least one herbicide of the sulfonylurea type that is suspended in a non-aqueous liquid phase, and (c) at least one non-ionic or anionic, surface-active substance or a mixture of the non-ionic and anionic substances.

Grass herbicides which may be used in accordance with the invention belong especially to the chemical classes of acetanilides, phenoxypropionic acids, pyrimidinyloxybenzoic acids, phenylsulfonyltriazoles, oxyacetamides, oxazolidindiones, phenylbenzamides, pyrimidinyl thiophthalides and indanes, and are preferably pretilachlor, cyhalofop, pyriminobac, cafenstrole, mefenacet, fentrazamid, oxaziolomefon, pentoxazone, etobenzanid, indanofan as well as epoprodan and the compound of formula I



These grass herbicides may also be used in a mixture together. They exist in dissolved or dispersed form in a non-aqueous liquid phase. The herbicides of the sulfonylurea type are also dispersed in preferably the same non-aqueous liquid phase. These are preferably cinosulfuron, pyrazosulfuron, bensulfuron, azimsulfuron, imazosulfuron, ethoxysulfuron, cyclosulfamuron or halosulfuron or mixtures thereof.

The preferred non-aqueous liquid phases include all vegetable and mineral oils, such as rapeseed oil, soybean oil, sunflower oil, castor oil, pine oil, cottonseed oil, as well as

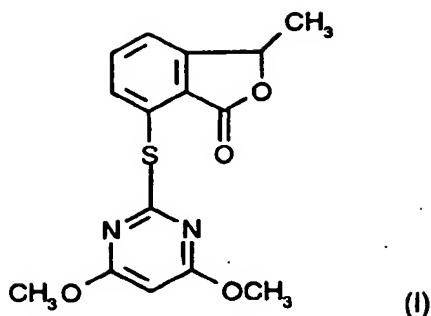
derivatives of these oils, for example esters, especially methylesters of these oils, as well as paraffinic and aromatic mineral oils, such as Orchex 796, Shellsol types, Isopar types, aromatic fractions, such as Solvesso 200 and esters such as Exxate 700, as well as mixtures thereof.

The non-ionic and anionic surface-active substances may be conventional, commercially available substances, for example ethoxylated vegetable oils such as Emulsogen EL, ethoxylated fat alcohols such as Genapol O-050, ethoxylated alkylphenols such as Synperonic NP8, ethoxylated polyethylene glycols or polypropylene glycols, e.g. Pluronic types, ethoxylated tristyrylphenol derivatives such as Soprophor 4D384 or Soprophor S/25, oleyl polyglycol ethers such as Genapol U-050, and silicone surfactants such as Silwet L77, as well as dodecylbenzene sulfonates such as Sermul 88A, alcohol ether sulfonates such as Genapol LRO, lignin sulfonates such as Ultrazin NA, phenol sulfonates such as Sipragil GN and polycarboxylates such as Geropon TA72, sulfonated naphthalene/formaldehyde condensates such as Supragil MSN, sulfosuccinates such as Aerosol OT 70 PG, polyacrylate derivatives such as Atlox 4913, maleic acid/olefin copolymers such as Sokolan CP9, alkyl polyglycosides, alkyl succinic acid anhydride derivatives, sorbitan esters, ethoxylated sorbitan esters, alkyl and alkylaryl polyglycol ether phosphoric acid esters and ethoxylated fatty acid esters, as well as taurides such as Hostapon T hk.

The above-mentioned herbicides are described in the Pesticide Manual, Eleventh Edition, British Crop Protection Council, 1997. The compound of formula I is known from EP-A-447506, fentrazamid from British Crop Protection Conference Proceedings, 1997, 67-72, and oxaziclomefon from British Crop Protection Conference Proceedings, 1997, 73-80.

Preferred herbicidal compositions according to the present invention contain as the grass herbicide cyhalofop, pyriminobac, cafenstrole, mefenacet, fentrazamid, oxaziclomefon, pentoxazone, etobenzanid, indanofan, epoprodan, pretilachlor or a compound of formula I

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or mixtures thereof.

As the herbicide of the sulfonylurea type, the compositions according to the invention preferably contain pyrazosulfuron, bensulfuron, azimsulfuron, imazosulfuron, ethoxysulfuron, cyclosulfamuron, halosulfuron or cinosulfuron or mixtures thereof.

The non-aqueous liquid phases to be used are preferably mineral oils or vegetable oils, or also mixtures thereof. The preferred non-ionic, surface-active substances that may be considered are ethoxylated vegetable oil, ethoxylated fat alcohol, ethoxylated alkylphenol, ethoxylated polyethylene glycol and polypropylene glycol and copolymers thereof, ethoxylated tristyrylphenol derivative, oleyl polyglycol ether or silicone surfactant, and the anionic surface-active substance may be a dodecylbenzene sulfonate, sulfosuccinate, ethoxylated tristyrylphenol sulfate or phosphate, alcohol ether sulfonate, lignin sulfonate, ethoxylated phenol sulfonate or polycarboxylate.

- A significant composition is one which contains as the grass herbicide pretilachlor or the compound of formula I or a mixture thereof suspended or dissolved in a vegetable oil, as the herbicide of the sulfonylurea type bensulfuron, pyrazosulfuron, azimsulfuron, imazosulfuron or cinosulfuron or mixtures thereof suspended in a vegetable oil, and as the surface-active substance a mixture of non-ionic and anionic compounds. Of these, preference is given to a composition which contains as the grass herbicide the compound of formula I suspended or dissolved in a vegetable oil, as the herbicide of the sulfonylurea type cinosulfuron suspended in a vegetable oil, and as the surface-active substance a mixture of non-ionic and anionic compounds. Of these, further preference is given to a composition which contains as the grass herbicide pretilachlor suspended or dissolved in a vegetable oil, as the herbicide of the sulfonylurea type cinosulfuron suspended in a

vegetable oil, and as the surface-active substance a mixture of non-ionic and anionic compounds.

An especially effective composition contains as the grass herbicide pretilachlor or the compound of formula I or a mixture thereof, preferably the compound of formula I alone, suspended or dissolved in rapeseed oil or rapeseed oil methyl ester or in a mixture thereof, as the herbicide of the sulfonylurea type bensulfuron suspended in rapeseed oil or rapeseed oil methyl ester or in a mixture thereof, and as the surface-active substance a mixture of a non-ionic with an anionic compound selected from castor oil ethoxylate, dodecylbenzene sulfonate, ethoxylated tristyrylphenol sulfate and oleyl polyglycol ether.

The compositions according to the invention have the great advantage that they may contain the herbicidal active ingredients in high concentrations, and that they remain protected from decomposition over a longer period of time. They also offer the possibility that other oil-soluble or liquid admixtures may be added without problems, such as additives that are suitable for increasing the biological activity, as well as stabilisers such as epoxidised vegetable oils. Surprisingly, the compositions according to the invention show practically no damage to the crops of cultivated plants after their application, despite using organic liquids.

The compositions according to the invention are preferably suitable for the control of weeds in flooded paddy fields. The process is advantageously carried out in such a way that the required amount of composition is mixed with the same amount or up to ten times the amount of water, and applied directly to the already flooded paddy field, or is added to the water flowing in during flooding of the paddy field (so-called splash application).

Furthermore, it is also possible, to apply the composition dropwise or in portions simultaneously with the mechanical planting of the rice plants (so-called dip application). Spray application of the composition according to the invention is similarly possible, but requires a higher dilution with water.

The application rates of composition according to the invention may vary within a wide range. It is preferable to use 50 to 2000 g/ha herbicide (grass herbicide plus herbicide of the sulfonylurea type).

The liquid compositions according to the invention contain per litre preferably 30 to 1920 g grass herbicide and 20 to 80 g herbicide of the sulfonylurea type, as well as 50 to 300 g of surface-active substance (anionic plus non-ionic). Normally, 2 - 20 l/ha of the formulations described below by way of example are required for direct application or for splash application. For spray application, this amount is usually 20 - 500 l/ha. The compositions according to the invention may also contain further customary additives, for example inert carriers such as kaolin and chalk, stabilisers, anti-foaming agents, preservatives, viscosity regulators, thickeners such as silicic acid or bentonite, binders, tackifiers, as well as fertilisers or other active ingredients. The compositions are produced in known manner, e.g. by intimately mixing and/or grinding the active ingredients with the formulation excipients and with liquid or solid carriers. Particularly preferred formulations are made up as follows:

Formulation examples

Substance	Trade name	function	conc. g/l
F1:			
Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180
bensulfuron methyl	Londax	active ingredient	51
castor oil ethoxylate 18EO	Alkamuls R/81	surface-active substance	80
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	50
rapeseed oil methyl ester	Edenor ME-SU	non-aqueous liquid phase	20
rapeseed oil		non-aqueous liquid phase	remainder to make up 1 l

F2:

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Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180
bensulfuron methyl	Londax	active ingredient	51
ethoxylated tristyrylphenol sulfate	Soprophor 4D384	surface-active substance	20
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	40
oleyl polyglycol ether	Genapol U-050	surface-active substance	90
mineral oil	Orchex 796	non-aqueous liquid phase	remainder to make up 1 l

F3:

Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180
bensulfuron methyl	Londax	active ingredient	51
ethoxylated tristyrylphenol sulfate	Soprophor 4D384	surface-active substance	20
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	50
castor oil ethoxylate 18EO	Alkamuls R/81	surface-active substance	80
rapeseed oil methyl ester	Edenor ME-SU	non-aqueous liquid phase	remainder to make up 1 l

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F4:

Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180
bensulfuron methyl	Londax	active ingredient	51
castor oil derivative	Marlowet LVS	surface-active substance	150
rapeseed oil		non-aqueous liquid phase	remainder to make up 1 l

F5:

Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180
bensulfuron methyl	Londax	active ingredient	30
azimsulfuron	Gulliver	active ingredient	6
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	50
castor oil ethoxylate	Sermul EN24	surface-active substance	50
silicic acid	Aerosil 200	thickener	20
rapeseed oil		non-aqueous liquid phase	234
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 1 l

F6:

Compound of formula I		active ingredient	180
pretilachlor	Rifit, Solnet	active ingredient	180

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bensulfuron methyl	Londax	active ingredient	30
azimsulfuron	Gulliver	active ingredient	6
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	65
castor oil ethoxylate	Sermul EN24	surface-active substance	65
tristyrylphenol ethoxylate	Soprophor BSU	surface-active substance	20
silicic acid	Aerosil 200	thickener	30
rapeseed oil		non-aqueous liquid phase	174
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 11

F7:

Compound of formula I		active ingredient	180
clinosulfuron	Setoff	active ingredient	24
ethoxylated tristyrylphenol sulfate	Soprophor 4D384	surface-active substance	20
castor oil ethoxylate	Sermul EN24	surface-active substance	40
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	40
silicic acid	Aerosil 200	thickener	40
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 11

F8:

Compound of formula I	active ingredient	180
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cinosulfuron	Setoff	active ingredient	24
ethoxylated tristyrylphenol sulfate	Soprophor 4D384	surface-active substance	20
castor oil ethoxylate	Sermul EN24	surface-active substance	65
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	65
silicic acid	Aerosil 200	thickener	40
aluminium silicate	Attagel 50	inert carrier	30
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 1 l

F9:

pretilachlor	Rifit	active ingredient	450
cinosulfuron	Setoff	active ingredient	24
ethoxylated tristyrylphenol sulfate	Soprophor 4D384	surface-active substance	20
castor oil ethoxylate	Sermul EN24	surface-active substance	60
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	60
aluminium silicate	Kaolin	inert carrier	250
silicic acid	Aerosil 200	thickener	30
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 1 l

F10:

pretilachlor	Rifit	active ingredient	450
cinosulfuron	Setoff	active ingredient	24

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ethoxylated tristerylphenol sulfate	Soprophor 4D384	surface-active substance	20
castor oil ethoxylate	Sermul EN24	surface-active substance	60
dodecylbenzene sulfonate	Sermul EA88	surface-active substance	60
aluminium silicate	Kaolin	inert carrier	200
silicic acid	Aerosil 200	thickener	30
rapeseed oil methyl ester	Agrimul 2232 F	non-aqueous liquid phase	remainder to make up 1 l

Application examples

Formulations F1, F2, F3, F4, F5, F6, F7, F8, F9 and F10 are diluted with water to 5 litres, and introduced directly to a flooded paddy field at an application rate of 5 l/ha (splash application). 22 days after application, control of the weeds *Echinochloa*, *Scirpus* and *Monochoria* is investigated, as well as the phytotoxic activity of the compositions on rice (100% indicates complete control of the weeds or completely withered rice, 0% indicates no control of the weeds or no phytotoxic activity on the rice). This takes place in tests running in parallel: a) upon emergence, b) at the 2.5 leaf stage and c) at the 4.1 leaf stage of *Echinochloa*. The results obtained in these tests are summarised in the following Table:

Formulation		% weed control		
		% phytotoxic activity		
		a)	b)	c)
F1	rice	0	5	11
	<i>Echinochloa</i>	99	96	95
	<i>Scirpus</i>	98	92	94
	<i>Monochoria</i>	100	95	95
F2	rice	0	7	9
	<i>Echinochloa</i>	99	98	92

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F3	Scirpus	98	94	94
	Monochoria	100	94	93
	rice	3	8	9
	Echinochloa	100	95	93
	Scirpus	99	90	95
	Monochoria	100	89	96

Formulation		% weed control	
		% phytotoxic activity	
		a)	b)
F5	rice	0	0
	Echinochloa	100	70
	Scirpus	90	80
	Monochoria	95	90
F6	rice	0	0
	Echinochloa	100	80
	Scirpus	90	80
	Monochoria	98	90
F7	rice	0	0
	Echinochloa	98	70
	Scirpus	70	80
	Monochoria	90	90
F8	rice	0	0
	Echinochloa	98	70
	Scirpus	70	90
	Monochoria	95	90
F9	rice	0	0
	Echinochloa	100	20
	Scirpus	98	90
	Monochoria	100	95
F10	rice	0	0
	Echinochloa	100	10
	Scirpus	95	90

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Monochoria

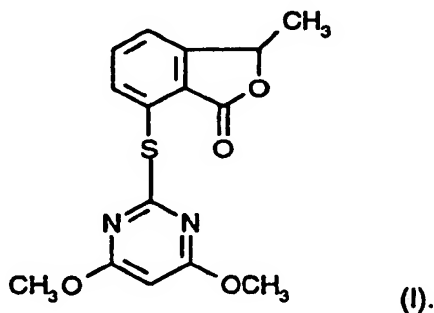
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The same results are obtained if these formulations are diluted with water, e.g. to 2 - 500 l.

What is claimed is:

1. Liquid herbicidal composition, containing
 - (a) at least one grass herbicide that is suspended or dissolved in a non-aqueous liquid phase
 - (b) at least one herbicide of the sulfonylurea type that is suspended in a non-aqueous liquid phase, and
 - (c) at least one non-ionic or anionic, surface-active substance or a mixture of the non-ionic and anionic surface-active substances
2. Composition according to claim 1, containing as the grass herbicide cyhalofop, pyriminobac, cafenstrole, mefenacet, fentrazamid, oxaziclomefon, pentoxazone, etobenzanid, indanofan, epoprodan, pretilachlor or a compound of formula I



or a mixture thereof.

3. Composition according to claim 1, containing as the herbicide of the sulfonylurea type pyrazosulfuron, bensulfuron, azimsulfuron, imazosulfuron, ethoxysulfuron, cyclosulfamuron, halosulfuron or cinosulfuron or a mixture thereof.
4. Composition according to claim 1, containing as non-aqueous liquid phase a vegetable or mineral oil or a mixture of these oils.
5. Composition according to claim 1, containing as the non-ionic, surface-active substance, an ethoxylated vegetable oil, ethoxylated fat alcohol, ethoxylated alkylphenol, ethoxylated polyethylene glycol or propylene glycol or copolymers thereof, ethoxylated tristyrylphenol derivative, oleyl polyglycol ether or silicone surfactant, or as the anionic surface-active

substance, a dodecylbenzene sulfonate, sulfosuccinate, ethoxylated tristyrylphenol sulfate or phosphate, alcohol ether sulfonate, lignin sulfonate, ethoxylated phenol sulfate or polycarboxylate or a mixture of these non-ionic and anionic, surface-active compounds.

6. Composition according to claim 1, containing as the grass herbicide pretilachlor or the compound of formula I or a mixture thereof suspended or dissolved in a vegetable oil, as the herbicide of the sulfonylurea type bensulfuron, pyrazosulfuron, azimsulfuron, imazosulfuron or cinosulfuron or mixtures thereof suspended in a vegetable oil, and as the surface-active substance a mixture of non-ionic and anionic compounds.

7. Composition according to claim 6, containing as the grass herbicide the compound of formula I and as the herbicide of the sulfonylurea type cinosulfuron.

8. Composition according to claim 6, containing as the grass herbicide pretilachlor and as the herbicide of the sulfonylurea type cinosulfuron.

9. Composition according to claim 6, containing as the grass herbicide pretilachlor or the compound of formula I or a mixture thereof, suspended or dissolved in rapeseed oil or rapeseed oil methyl ester or in a mixture thereof, as the herbicide of the sulfonylurea type bensulfuron suspended in rapeseed oil or rapeseed oil methyl ester or in a mixture thereof, and as the surface-active substance a mixture of a non-ionic with an anionic compound selected from castor oil ethoxylate, dodecylbenzene sulfonate, ethoxylated tristyrylphenol sulfate and oleyl polyglycol ether.

10. Composition according to claim 9, containing as the grass herbicide the compound of formula I.

11. Use of the liquid herbicidal composition according to claim 1 in the control of undesired plant growth in crops of cultivated plants.

12. Use according to claim 11 for the control of undesired plant growth in rice crops by means of direct application of the composition to already flooded paddy fields, to paddy fields that are just being flooded, or during planting of the rice plants.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/08359

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 A01N47/36 A01N25/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 456 198 A (HODOGAYA CHEMICAL CO LTD ; TOHO CHEM IND CO LTD (JP)) 13 November 1991 (1991-11-13) claims 4-6	1-12
A	EP 0 768 034 A (CIBA GEIGY AG) 16 April 1997 (1997-04-16) claims	1-3, 6-10
A	FR 2 605 497 A (CIBA GEIGY AG) 29 April 1988 (1988-04-29) claims	1-3, 6, 8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/08359

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